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Manufacturing Technology of All-solid-state Thin-film Lithium Secondary Battery for Stand-alone MEMS/Sensor Applications

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Abstract

All-solid-state thin-film lithium secondary battery has come to be recognized as one of the key enabling technologies for stand-alone MEMS/Sensor devices which are essential for internet of things (IoT) solution.

A detailed explanation will be given on the vacuum technologies such as sputtering for the manufacturing of thin-film lithium secondary battery, in which we have successfully established reliable hardware and process technologies as mass-production technology for manufacturing thin-film lithium secondary battery.

1. Introduction

Lithium ion secondary batteries have particularly high energy density and do not degrade easily by repeated charge and discharge cycles, and there has been a steady increase in the demand for lithium ion secondary batteries especially for consumer electronics. However, lithium ion batteries even have the risks of leakage and fire caused by organic liquid electrolyte. To resolve these problems essentially, all-solid-state type battery that uses solid electrolyte has been proposed and developed.

Among the all-solid-state batteries, thin-film lithium secondary batteries (TFBs) are produced by thin-film deposition technologies which have special advantages that are not only safe as their being all-solid-state but also thin, small, lightweight and flexible [1]. As solid electrolyte, glassy lithium phosphorus oxynitride (LiPON) thin film has been used commonly due to advantages of no grain-boundary, isotropic property, less electronic conductivity and electrochemical stability [2].

Accordingly, it is expected they can be employed in various electronic devices such as RF-ID tag and smartcard as well as emerging MEMS-IC and wireless sensor which are expected to be used for stand-alone MEMS/sensor applications in combination with various energy harvesters such as thermal, vibration/motion, ambient light and rf electromagnetic wave [3]. The low power consumption of silicon-based electronics has enabled a broad variety of battery-powered handheld, wearable and even implantable devices. All these devices need a compact and lightweight energy source, which enables the desired portability and energy autonomy [4].

2. Manufacturing technology of thin-film lithium secondary battery

Figure 1 shows the schematic drawing of TFB [5]. TFB is fabricated by forming each layer (i.e. cathode, electrolyte, anode and current collectors) mainly using physical vapor deposition techniques [6].

In our manufacturing sputtering system, planar-type magnetron sputtering is employed for the deposition of the cathode and solid electrolyte layers, which are the major components of the battery. Lithium cobalt oxide ($LiCoO_2$; LCO) and lithium phosphate (Li_3PO_4 ; LPO) are used for sputtering targets with 300 mm in diameter. Cathode layer is thicker and requires higher deposition rate than other layers. Using high-quality LCO target and RF+DC hybrid sputtering technique, we successfully achieved high deposition rate with exceeding 100 nm/min. Meanwhile, LiPON electrolyte layer is deposited using LPO target and RF reactive sputtering technique with nitrogen gas. It has been confirmed that the ion conductivity of sputtered LiPON film is no less than 1e-6 S/cm at room temperature [7].

Vacuum evaporation technique is employed for deposition of lithium anode. Our vacuum evaporation system is equipped with a crucible with lamp heater, substrate holder and quartz crystal microbalance as deposition rate detector.

Manufacturing flow of TFB is as follows [8,9].

(1) Sputtering Pt/Ti layer onto the substrate as a cathode current collector.
(2) Sputtering LCO layer onto Pt/Ti layer.
(3) Annealing at about 600deg.C for LCO crystallization.
(4) Sputtering LiPON layer onto LCO layer.
(5) Sputtering Ni/Cr layer onto the substrate as an anode current collector.
(6) Evaporating lithium onto LiPON and Ni/Cr
(7) Packaging (Sealing layer) onto above stack structure.

All layers from (1) to (7) are deposited using shadow mask for patterning, and sample is kept at low-dew-point ambient until packaging.

TFB is fabricated basically with 3-μm-thick LCO, 2-μm-thick LiPON and 2-μm-thick lithium. Designed battery capacity is around 0.2 mAh.

3. Battery performance of manufactured battery

Various properties are investigated on our practical TFB. Charging method is CC/CV (constant current/constant voltage) mode and charging current is set to 0.3 mA (current density is 0.21 mA/cm^2). Cut-off voltage and current are set to 4.2 V and 0.03 mA, respectively. Discharging method is CC mode, discharging current is set to 0.3 mA, and cut-off voltage sets to 3.0 V. Figure 2 shows charge/discharge cycle performance of TFB. Discharge capacity is normalized with 100% depth of discharge and indicates over 95% of initial value even after 1,000 charge/discharge cycles. In conventional lithium ion battery (polymer), it has been reported that the capacity is about 80% of initial value after 500 cycles. It is considered that the reason for good cycle performance of TFB is owing to higher electrochemical stability of LiPON than conventional organic liquid electrolyte.

Figure 3 shows discharge curve under each current condition (C-rate performance). Discharge current of 0.3 mA corresponds to 1C as theoretical value, and that means the reference discharge current will discharge the entire battery in 1 hour. Discharge capacity at 0.3 mA is 200 µAh, whereas at 5.0 mA, 145 µAh, which is approximately 72 % of 0.3 mA. If cut-off voltage is changed to 2.0 V, the battery can discharge at 12 mA, and discharge capacity is 120 µAh, which is approximately 60 % of 0.3 mA. It is confirmed that fabricated battery had good performance and can drive at high C-rate.

We also try to confirm reliability of fabricated battery. Figure 4(a) shows the nailing test that fabricated battery is nailed and short-circuited. It is confirmed that there are no problem such as fire and thermal runaway. Figure 4(b) shows that driving of LCD by "bended" battery (r=15 mm). LCD can be successfully driven and indicates battery's voltage across terminals.

4. Conclusions

Manufacturing technologies such as production tools and fabrication processes for TFB are introduced and also performance of fabricated practical battery was investigated. They have special advantages that are not only safe as all-solid-state, but also thin, small, lightweight and flexible with excellent performance. So they can be employed in various small electronic devices especially for stand-alone MEMS/Sensor applications. We hope we will be able to contribute to realization of IoT solutions and growing of their market through our manufacturing technology for the battery.

References

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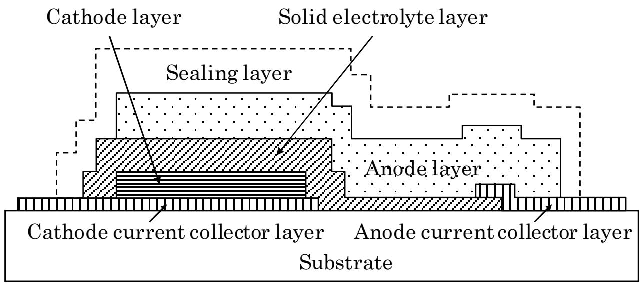

Fig. 1. Schematic drawing of TFB.

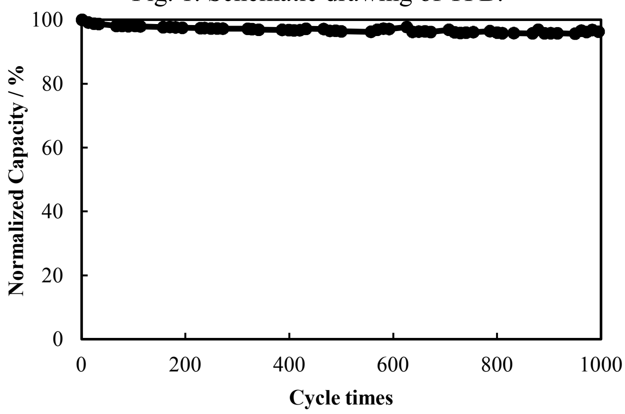

Fig. 2. Charge/discharge cycle performance of TFB.

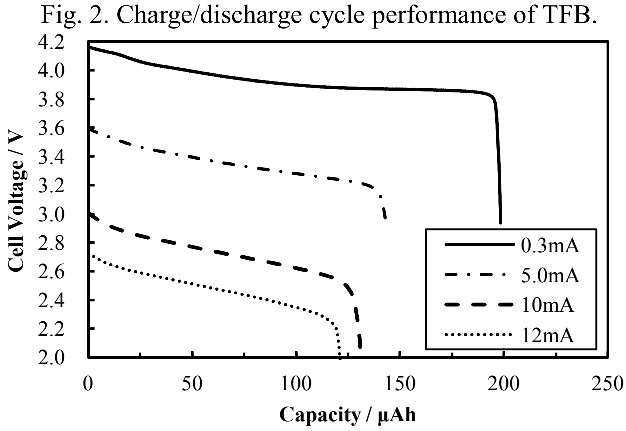

Fig.3. C-rate performance of TFB.

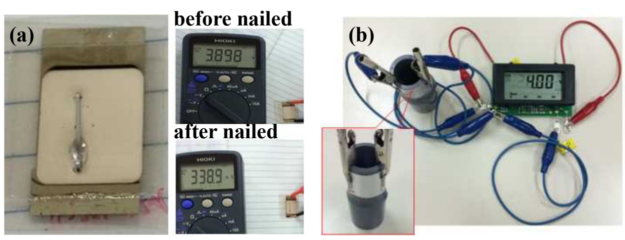

Fig.4. Appearance of reliability test;
(a) Nailing test, (b) LCD driving test by bended battery.